Colloid Polym Sci (2013) 291:1683–1691
DOI 10.1007/s00396-013-2903-3

ORIGINAL CONTRIBUTION

Synthesis of polyampholyte microgels from colloidal salts of pectinic acid and their application as pH-responsive emulsifiers

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Received: 12 October 2012 / Revised: 29 December 2012 / Accepted: 4 January 2013 / Published online: 17 January 2013

Abstract A novel method for obtaining cross-linked microgels of apple pectin has been introduced. This method is based on the Ugi four-component condensation in colloidal suspensions of pectinic acid and amines. Using various processing parameters (the polysaccharide concentration, the type and density of crosslink, and the optimal pH range), particles with controlled colloidal properties have been obtained. Lightly cross-linked polysaccharide chains acquire anionic character due to deprotonation of the carboxyl groups at pH9–10. Increasing the degree of cross-linking leads to a polyampholyte microgel, which can be protonated in acidic medium or deprotonated in basic medium. Polyampholyte microgels derived from apple pectin have proved to be an effective Pickering emulsifier at low concentrations and pH2–3, forming stable oil-in-water emulsions. These Pickering emulsions exhibited pH-responsive behavior: raising the solution pH to 10 resulted in immediate demulsification due to the destabilization of microgel network at the oil–water interface.

Keywords Apple pectin · Pectinic acid · Colloids · Ugi reaction · Microgel · Emulsion

Introduction

Nanoparticles of hydrogels are presently under intense investigation for drug delivery, tissue engineering, and surface coatings [1, 2]. Hydrophilic microgels can be defined as the swollen particles within the generally accepted colloidal range of 10 nm to 1 μm, which can absorb and retain large amounts of water. The great water content in a hydrogel and the ability for architecture control via cross-link density determine the unique properties of this material, such as good biocompatibility and controlled transfer of various compounds in and out of the gel [3]. In the last years, most attention was paid to polyampholyte microgels, which belong to smart materials due to their response to temperature, pH, ionic strength, water–organic solvent composition, electric field, etc. Various microgels bearing amino and carboxyl groups have been obtained on the basis of synthetic and natural polymers [4–6] including polysaccharides [7, 8].

Pectin is a heteropolysaccharide existing in the primary cell walls of all higher terrestrial plants as an important structural element [9]. The main component of natural pectin is α (1→4) linked D-polygalacturonic acid, which is partially esterified with methanol. The various raw materials (apples, citrus fruits, sugar beet, and sunflower) can yield a number of different types of pectin with specific properties. Generally, pectin is widely used as a natural gelling and stabilizing substance in many products, mainly in the food industry, but also in the non-food sector [10]. One of most interesting types of pectin is sugar beet pectin, which has unusual emulsifying properties and is currently used for stabilization of the oil–water interfaces in many food products [11]. Taking into account the great importance of emulsions for various industrial sectors, it seems likely that eco-friendly emulsifiers on the basis of polysaccharides will become more popular in the future.

Macrogels can be obtained from solutions of low-methoxyl pectin at concentrations superior to the critical concentration of chain entanglement (C^*) by increasing interactions between macromolecular chains [12]. Two general approaches were used here: precipitation of pectin by decreasing the pH of the solution with mineral acids [13] or cross-linkage of

Electronic supplementary material The online version of this article (doi:10.1007/s00396-013-2903-3) contains supplementary material, which is available to authorized users.

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polymer chains with calcium ion, polyamines, or glutaric aldehyde [14, 15]. The Ugi multicomponent reaction was also applied to the formation of chemically cross-linked macrogels of apple pectin [16] and other polysaccharides [17]. However, only a few from these methods are suitable for obtaining pectin microgels at concentrations close to C^* [18, 19].

It was revealed recently that the formation of colloidal aggregates in polysaccharide solutions enhanced their emulsifying properties [20]. In general, colloidal particles act in many ways like surfactant molecules, particularly if adsorbed to the interface of emulsion droplets [21]. However, important differences exist between the solid particles and soft microgels, due in part to the fact that microgels form elastic interfacial layers, which consist of clusters with uncovered areas in between [22]. Recently, atomic force microscopy has been used to define the structure of thin films transferred from the oil–water interface of oil droplets immersed in a solution of a polysaccharide extract of sugar beet pectin [23]. According to this investigation, at the lowest pectin concentration (0.1 %) some large holes are visible within the layer, while at higher concentration (2 %) the layer presents asperities. The authors of this work suggested that the observed protrusions are aggregates formed in bulk solution of pectin before adsorption to the interface. However, to our knowledge, stabilization of emulsions using cross-linked pectin microgels has not been described.

We report herein a facile synthesis of polyampholyte microgels on the basis of apple pectin and preliminary investigation of their emulsifying properties. Various processing parameters such as polysaccharide concentration, the type and density of crosslink, and the optimal pH range were optimized to yield a well-designed colloid system. The main objectives of our study were to reveal the distinctive features of polyampholyte microgels derived from apple pectin. This approach opens the way to rational design of novel emulsifiers on the basis of natural polysaccharides.

Materials and methods

Materials

A low-methoxyl apple pectin sample, Pectin Classic AU 701, was purchased from Herbstreith & Fox GmbH (Neuenburg, Germany) and its structural parameters were determined in our laboratory: the degree of esterification (DE) was 38.5 mol%, and the average molar mass (M_w) was 54 kDa with the broad distribution of molecular weight. The critical concentration of chain entanglement, C^*, is approximately 0.5 wt.% [16]. 1,4-Bis(3-isocyanopropyl)piperazine was synthesized according to the well-known protocol [24]. Benzylamine, 4-fluorobenzylamine, and furfurylamine were purchased from Acros Organics (Germany). 4-Picolylamine, 3-(diethylamino)propylamine, and 1,4-bis(3-aminopropyl)piperazine were purchased from Aldrich Chemical Co. (USA). All reagents with the exception of pectin were of analytical grade and were used without additional purification.

Pectinic acid synthesis

Pectin (10 g) was dissolved under moderate stirring and 40 °C in a 1 l of 0.1 M solution of NaOH during 90 min. The resulting mixture was treated with 0.1 M solution of HCl (pH=3), washed with deionized water, and centrifuged at 4,000×g for 30 min. The precipitate of pectinic acid was washed with acetone three times and centrifuged at 4,000×g for 30 min. Finally, the product was dried at room temperature under vacuum for 24 h to yield white powder of pectinic acid (5.6 g). The DE for this product was 1.5 mol% and the average molar mass M_w=47 kDa with the broad distribution of molecular weight.

Formation of the pectinic acid salts

Pectinic acid (0.1 g) was dissolved under moderate stirring in a 100 ml solution of Na_2CO_3 (35 mg) in deionized water and filtered through Millipore membrane (0.22 μm). The resulting mixture was treated with solution of benzylamine hydrochloride (40 mg) in 5 ml of deionized water. After 1 h under moderate stirring, the resulting solution was directly used for DLS measurement. All stages were performed at 25 °C.

Microgels synthesis

Typical procedure for obtaining of microgel with 15 % degree of substitution includes the following steps. (1) Pectinic acid (0.5 g) was dissolved under moderate stirring in a 500-ml solution of Na_2CO_3 (170 mg) in deionized water. The resulting mixture was treated with solution of benzylamine (300 μl) in 15 ml of 0.1 M HCl (0.5 molar ratio). After 10 min, cross-linking agent 1,4-bis(3-isocyanopropyl)piperazine (56 mg, 15 % substitution) was added to the solution and homogenized with manual shaking. (2) After 1 h, excess of formaldehyde (30 % solution in water, 300 μl) was added to the reaction mixture. The visible turbidity of the mixture was observed that was an indicator of the reaction rate. The pH of the solution should be in a range of pH=8–8.5 during all reaction times. (3) After 3 h, the reaction mixture was filtered through Millipore membrane (0.45 μm) and the resulting solution was directly used for DLS measurement. To obtain samples of pure microgels, 0.1 M solution of HCl was dropped into the reaction mixture until formation of macroscopic gel was observed, washed with deionized water, and centrifuged at 4,000×g for 30 min. The precipitate of microgel was washed with acetone three times and centrifuged at 4,000×g for 30 min. Finally, the product was dried at room

temperature under vacuum for 24 h to yield white powder of pectinic acid microgel (0.48 g). All stages were performed at 25 °C.

Microgels characterization

The particle size and zeta potential were measured using Zetasizer Nano SL (Malvern Instrument, UK) at scattering angle of 173°, 670 nm, and 25.2 °C. Polydispersity index was calculated from a Cumulants analysis of the DLS measured intensity autocorrelation function. PDI=$2a_2/(a_1)^2$ where a_1 is first moment (cumulant) and a_2 is second moment. The average hydrodynamic diameters were calculated by the non-negative least-squares (NNLS) method using Malvern General Purpose & Multiple Narrow Mode algorithm, which separated the different peaks at multimodal distribution.

IR spectra were recorded on a Bruker Alpha spectrometer. ^{1}H NMR spectra were recorded on a Bruker DRX-400 (400 MHz) spectrometer in D_2O at 70 °C. All samples were transformed into sodium salts before NMR measurement.

Emulsion characterization

The emulsion was obtained on the basis of 0.1 wt.% solution of cross-linked microgels derived from pectinic acid. These solutions (10 ml) were homogenized with 10 ml of toluene for 2 min at 20 °C using an IKA Ultra-Turrax T-18 homogenizer operating at 12,000 rpm. Emulsion stabilities after standing for 24 h at 20 °C were assessed by optical microscopy studies using OLYMPUS GX-71 microscope equipped with SIAMS Potolab program (100 individual droplets measurements).

Results and discussion

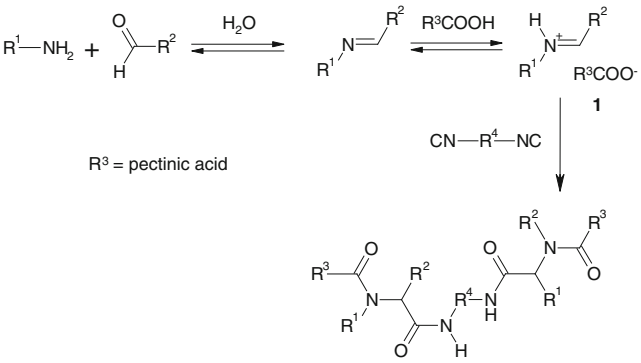
Synthesis of microgel

The aim of the synthesis effort in our investigation is to access pectin-based colloidal particles, which have an average hydrodynamic diameter in the range of 200–350 nm and narrow distribution of particle sizes. For this purpose, we have proposed a novel approach based on the Ugi multicomponent reaction in colloidal suspensions. Our research group demonstrated previously that a three-component Ugi reaction could be effectively conducted in diluted micellar solutions [25]. Therefore, we predicted that it would be possible to carry out this reaction in colloidal suspensions of pectin at concentrations below C^* (<0.5 wt.% [16]). The main advantage of the Ugi reaction for creation of colloidal particles is a stepwise character of particle formation, making it possible to control size and polydispersity. Its mechanism includes the formation of the iminium salt **1** between three initial reagents: amine, carbonyl compounds, and carboxylic acid (Scheme 1) [26]. At low concentrations of pectin, we expect appearance of colloidal agglomerates of salts with amines, which can be "frozen" after addition of a diisocyanide and formaldehyde. It should be noted that the Ugi multicomponent reaction can be accelerated up to 300-fold (compared to organic solvents) in water or in aqueous solutions of glucose [27]. Therefore, the formation of cross-links between the polymer chains is a very rapid process in this case.

Before synthesis of cross-linked microgel, we carried out the mild hydrolysis of the apple pectin to yield pectinic acid. As stated above, a low degree of esterification favors the strong interaction between polymer chains and makes possible agglomeration of pectin in diluted solutions. In addition, a low content of methoxy groups facilitates the determination of cross-linkage density using NMR spectroscopy. We did not observe remarkable changes in the degree of polymerization during this procedure. On the other hand, in contrast to the starting apple pectin, the samples of pectinic acid are totally insoluble in water at pH 1–4 and are able to form physical macrogel without an addition of calcium ion.

The first step of our synthesis was the formation of salts on the basis of pectinic acids and benzyl amine. For this purpose, all reagents were mixed together in distilled water at the concentration 0.25 wt.%. Dynamic light scattering measurement of this solution has confirmed the formation of the colloidal particles with a relatively broad distribution of particle sizes and average hydrodynamic diameter of 235 nm (Fig. 1). These data were in accordance with our initial suggestions concerning the nature of intermediates in the Ugi reactions with polysaccharides. Thus, the big particles are in equilibrium with smaller ones (30–50 nm), which cover the remaining polymer and small agglomerates in the bulk solution. Intensity of light scattering for these small particles is relatively low, despite their high content by volume (up to 40 %).

The second step was addition of an isocyanide and formaldehyde to the colloidal suspension of pectinic acid salt. To obtain a polyampholite microgel, we have selected an



Scheme 1 Mechanism of the Ugi reaction

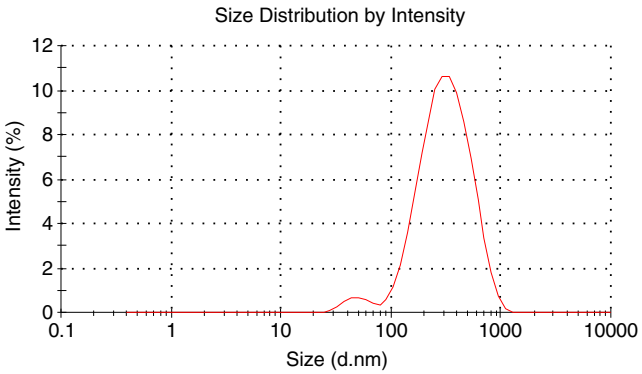
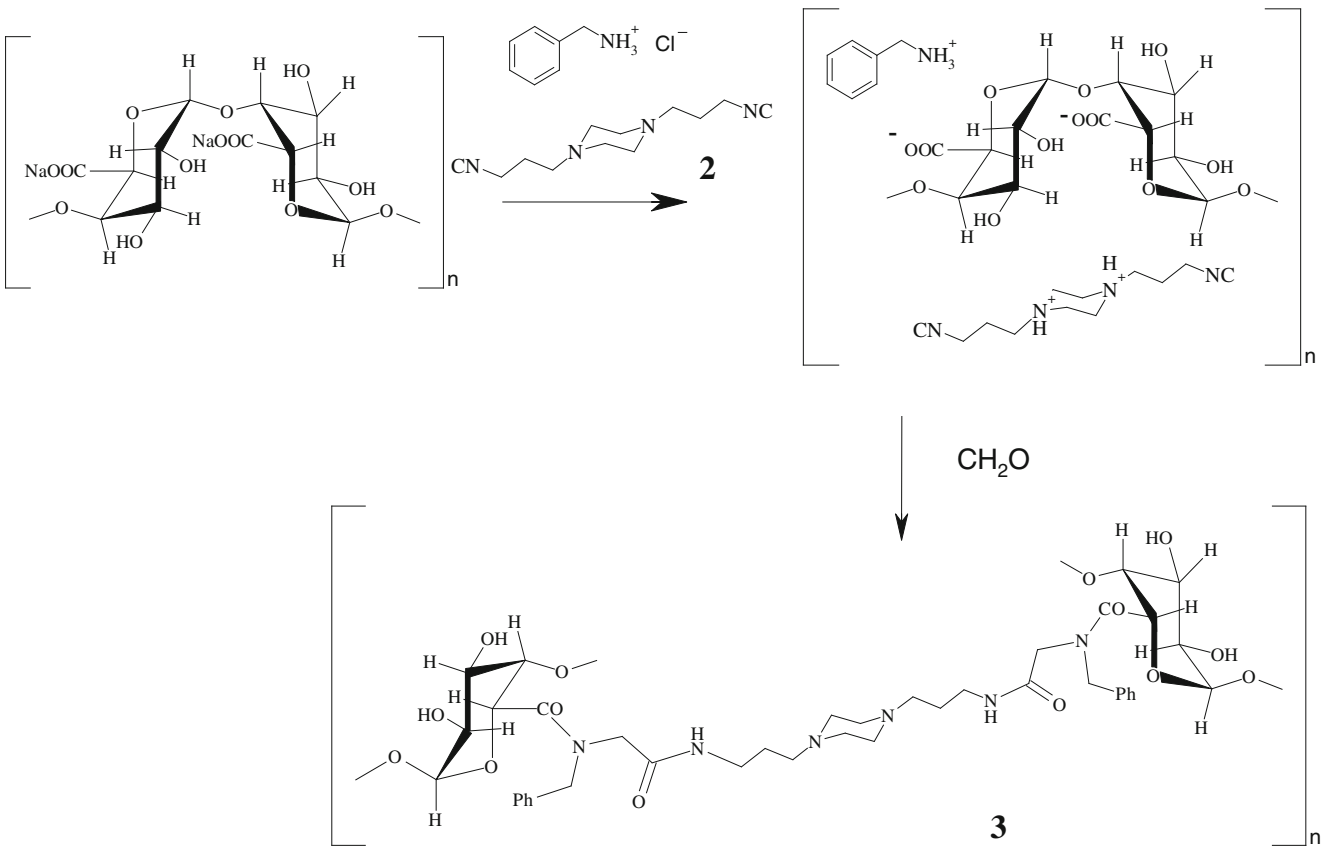


Fig. 1 Size distribution of pectinic acid–benzyl amine salt by intensity of light scattering

isocyanide having basic properties, that is 1,4-bis(3-isocyanopropyl)piperazine **2**. In this case, a mixed salt from this reagent, benzyl amine and pectinic acid, was formed, which made possible to carry out the Ugi reaction inside the microgel particles after the addition of formaldehyde (Scheme 2). The optimal concentration of pectinic acid for this synthesis was found as 0.1 wt.%. We have also used various concentrations of cross-linking agent from 8 to 40 mol% in this reaction, which opened the way to five samples of microgels **3a**–**e** with various cross-linkage densities (7 %, 15 %, 21 %, 27 %, and 33%). In all cases, stable colloid solutions having prominent opalescence have been obtained. In contrast, we have not observed the formation of macrogel in our system. This successful approach gives us an access to well-defined colloidal particles of microgel **3** having carboxyl and amino groups (Table 1).

Structural changes of pectinic acid after the Ugi reaction was confirmed by IR and NMR spectra. Thus, pectinic acid sodium salt has an absorption at 1,580 cm^{-1} ascribed to the carbonyl stretching vibration mode of carbonyl group in D-polygalacturonic acid, and a very weak absorption at 1,745 cm^{-1} due to the presence of the methoxy groups. After the Ugi reaction, the appearance of prominent bands at 1,662 and 1,535 cm^{-1} were observed, which were assigned to the carbonyl stretching vibration mode of secondary amide (amide band I) and the bending vibration mode of the amide band II, respectively. No absorptions in the range of 2,100–2,150 cm^{-1} were observed in the spectra of the cross-linked products, which would have been indicative of the existence of isocyano groups. Analysis of ^{1}H NMR spectra has confirmed that all of the main structural elements of starting materials were incorporated into the final product (see supporting information). Thus, piperazine ring can easily be identified by the presence of ^{1}H resonances in the range 2.40–2.55 ppm, while propyl group has



Scheme 2 Formation of the cross-linked microgels **3** on the basis of pectinic acid via the Ugi reaction

Table 1 Average hydrodynamic diameter and zeta potential of the microgel samples **3**–**7** at pH8.5 and pH2.0

Sample	Amine	Density of cross-linkage (%)	Average diameter of microgel (nm)		Zeta potential (mV)	
			pH8.5	pH2.0	pH8.5	pH2.0
3a	Benzylamine	6.9	287	Macrogel	−41	Macrogel
3b		15.0	361	Macrogel	−34	Macrogel
3c		21.3	303	Macrogel	−30	Macrogel
3d		26.7	239	226	−28	19
3e		32.1	235	240	−29	21
4a	Furfurylamine	14.9	278	Macrogel	−35	Macrogel
4b		27.6	241	235	−32	20
5a	4-Picolylamin	15.2	265	260	−34	19
5b		26.3	253	256	−31	28
6a	3-(Diethylamino) propylamine	14.8	292	311	−33	32
6b		26.5	260	267	−30	36
7a	4-Fluorobenzylamine	15.4	340	Macrogel	−34	Macrogel
7b		27.1	313	302	−27	18

three signals in the regions 1.50–1.72, 2.25–2.40, and 3.10–3.30 ppm. The presence of benzyl group can be confirmed by the signals of phenyl ring in the range 7.25–7.55 ppm. The signals of two methylene groups overlapped with the signals of polygalacturonic acid in the range 3.65–5.15 ppm. On the other hand, no signal of formamide group that may be a result of competing hydrolysis of isocyano group has been revealed in the spectra. In summary, the above results clearly showed that cross-linked pectinic acid were obtained and that the reaction was highly selective toward formation of an amide bond. After the termination of the reaction with addition of HCl, the excess of cross-linking agents [benzylamine and 1,4-bis(3-isocyanopropyl)piperazine] were removed by careful washing with 0.1 M HCl, water, and acetone. Therefore, the observed intensity of the signals of benzyl group and piperazine ring can be correlated directly with the yields in the Ugi reaction. For all samples **3a**–**e**, these were in the range 80–85 % which confirms the high effectiveness of this synthesis even in diluted solutions. This fact confirms our suggestion that the formation of the iminium salts **1** between all starting compounds provides high reaction rate of the Ugi reaction. In addition, cross-linkage density can be correlated with the quantity of diisocyanide up to 35 % degree of substitution. At higher concentrations, the yields were decreased and the presence of free isocyano group was detected.

Dynamic light scattering of the microgels **3a**–**e** allowed us to reveal the variation of the size and polydispersity index of colloidal particles. In contrast to the initial salts with benzylamine, the particles of microgel **3** after cross-linkage are characterized by a narrow distribution of hydrodynamic diameters. For all samples **3a**–**e** obtained in our investigation, polydispersity index was in the range 0.09–0.17 and no fractions of initial polymer were detected in the range 10–100 nm even at low concentrations (0.5 g/l) and high pH (8.5–9). The average hydrodynamic diameter of these particles was in the range of 240–360 nm depending on reaction conditions. The typical distribution of diameter by light scattering intensity for sample **3a** is shown in Fig. 2.

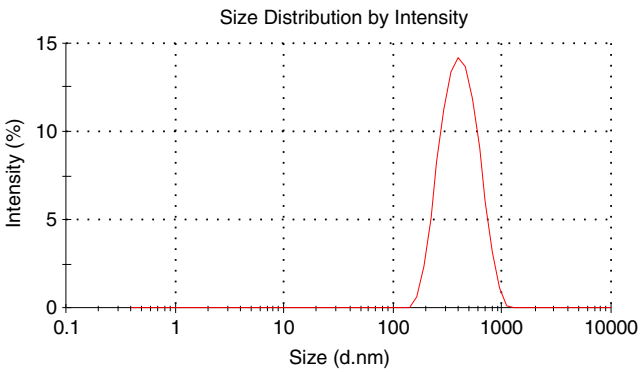


Fig. 2 Size distribution of cross-linked microgel **3a** by intensity of light scattering

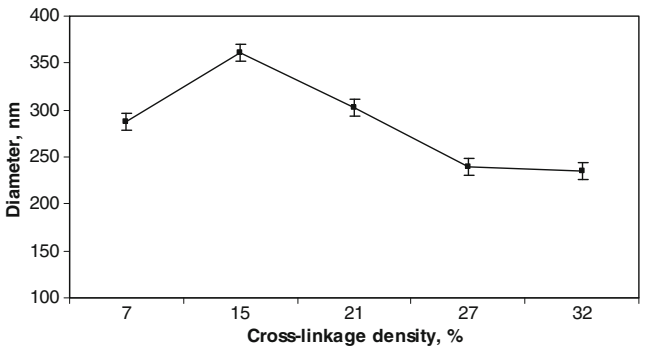


Fig. 3 Relationship between cross-linkage density and average hydrodynamic diameter of the microgels **3a**–**e** (pH8.5)

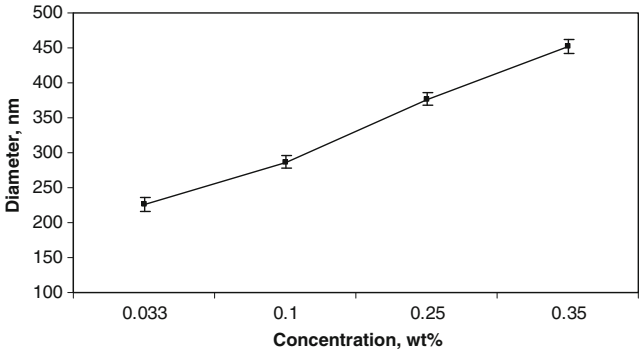


Fig. 4 Relationship between concentration of pectinic acid and size of the microgel **3a** (pH8.5)

An important parameter in the synthesis of the target microgels **3a**–**e** is the ratio of the cross-linkage agent 1,4-bis(3-isocyanopropyl)piperazine to the starting polysaccharide. We have defined the relationship between the hydrodynamic diameters of the colloidal particles and the molar degrees of cross-linkage in microgels at pH8.5 (Fig. 3). The resulting function has a maximum in the range of 12–18 mol% that is probably a result of the steric repulsion between substituted polymer chains. In that way, the colloidal particles with minimal diameter (ca. 250 nm) can be obtained using low (8–15 mol%) and high (30–40 mol%) quantity of the cross-linkage agent.

Size and size distribution of the nanoparticles derived from polysaccharides via a chemical or ionic cross-linkage depend largely on the concentration of the starting polymer in solution. In our investigation, we revealed a similar dependence (Fig. 4). It demonstrates that the hydrodynamic diameters of the cross-linked nanoparticles was mostly affected by the increased concentration of pectinic acid in solution, and the increase in size with concentration showed a relationship close to linear. Such dependence is observed only in diluted solutions at a concentration in the range of 0.02–0.4 wt.% at pH8.5. In the range of 0.4–0.5 wt.%, the instable colloidal solutions are formed, while the concentrations of pectinic acid >0.5 wt.% led to cross-linked macrogel. All colloidal suspensions of microgels were stable at pH8–10 during several months without increase in the particle size.

In continuation of our study, we have synthesized other eight samples of microgels **4a**,**b**, **5a**,**b**, **6a**,**b**, and **7a**,**b** using miscible with water furfurylamine, 4-picolylamine, and 3-(diethylamino)propylamine as well as water-soluble 4-fluorobenzylamine. In every case, two levels of cross-linkage density [15 % (**a**) and 27 % (**b**)] were selected (Table 1). It was found that the size of the nanoparticles cross-linked via the Ugi reaction depended largely on amine type. The sampling data presented in Table 2 show the decrease of the particle diameter with increase of the amine solubility. On the other hand, polydispersity index is much lower in the case of amines having high log *P*.

In summary, the Ugi reaction gives access to cross-linked microgel of pectinic acid in a workable manner. The size of colloidal particles can be regulated preciously using fixed concentration of pectinic acid and cross-linkage density. On the other hand, the property of the particle surface can be modified easily with the correct choice of amine component in the Ugi reaction. Thus, the free design of polyampholyte microgels is possible with this approach.

Microgel properties

Solubility of the microgels **3**–**7** in water depends on the density of amino groups. Thus, lightly cross-linked microgels **3a**,**b**, **4a**, and **7a** were easily dispersed in water at pH9–10, while lowering the solution pH of the aqueous phase to pH2–3 with aqueous HCl led to the formation of the physical gel precipitate. In contrast, other microgels **3c**–**e**, **4b**, **5**, **6**, and **7b** flocculated only within the short pH range (isoelectric-point region) owing to the neutralization of the positive and negative charges. From the chemical structure of these samples, it is expected that the amino groups of cross-links can be protonated in acidic medium and possess a positive charge, while the residual free carboxyl groups of polysaccharide chains can be deprotonated in basic medium and possess a negative charge. This result was confirmed by measurements of zeta potential for the microgel samples **3**–**7** (Table 1). For example, microgel **5b** showed a positive potential below pH5.0 (up to 28 mV), and its potential became negative above pH6.5 (up to −31 mV). In the pH range 5.6–5.8, zeta potential approached zero and the microgel formed the physical gel precipitate. However, the flocculated microgels could be easily redispersed by either an increase or a decrease in pH of the medium. We have found that the hydrodynamic diameters of microgels **3c**–**e**, **4b**, **5**, **6**, and **7b** at pH2 and pH8.5 are almost the same, which is

Table 2 Average hydrodynamic diameter, log *P*, and polydispersity index of the microgel samples with 15 % cross-linking density (pH8.5)

Sample	Amine	log *P*[a]	Average diameter of microgel (nm)	PDI
4a	Furfurylamine	−0.31	278	0.23
5a	4-Picolylamin	−0.40	265	0.24
6a	3-(Diethylamino) propylamine	0.13	292	0.20
3b	Benzylamine	1.09	361	0.14
7a	4-Fluorobenzylamine	1.24	340	0.15

[a]Data from ACD/Labs database

an evidence of the swollen state of the microgels (Table 1). This result is quite similar to the behaviors observed in the cases of other polyampholyte polymers and their gels [4, 8].

Microgels of pectinic acid obtained via the Ugi reaction **3**–**7** were used as model compounds for evaluation of possible mechanism of the oil-in-water emulsions stabilization with polysaccharide emulsifiers. We have succeeded in obtaining emulsions with highly substituted (more than 15 % amino groups) microgels **3c**–**e**, **4b**, **5a**,**b**, **6a**,**b**, and **7b** as the Pickering-type emulsifiers at concentrations in the range of 0.5–1.5 g/l. Various solvents were used as follows: heptane, crude oil, benzene, toluene, and chloroform. Between them, toluene was selected as a model solvent. Our experiments using polyampholyte microgels confirmed that stable toluene-in-water emulsions were formed only at pH2–3. The drop test indicated that oil-in-water (o/w) emulsions were obtained in all cases. Presumably, this is related to the high wettability of the cross-linked microgels in aqueous phase. Optical microscopy studies revealed spherical oil droplets with the broad distribution of their diameters (Fig. 5). The average oil droplet diameters measured using a SIAMS Potolab program after 24 h were in the range of 14–62 μm. Selected data with toluene, heptane, and chloroform as a solvent is presented in Table 3. Thus, these emulsions are practically identical to the one previously obtained with synthetic microgels as a particle emulsifier [28]. It should be noted that in contrast to sugar beet pectin, the surface tension of the low-methoxy apple pectin solutions is high (close to surface tension of water) at low concentrations (<1 %) [29, 30]. Therefore, drastic changes in emulsifying properties of this polymer can be accounted to the formation of microgel particles during the Ugi reaction.

The main factor having influence on the stability of the obtained emulsions is pH of aqueous phase. Thus, the stable emulsions, which could be stored at room temperature during 1 month and more, were obtained in acidic continuous phase (pH2–4). For example, the toluene-in-water emulsions prepared using cross-linked microgel of pectinic acid **5b** were demulsified by raising the solution pH of the aqueous phase to pH9–10 with aqueous NaOH, followed by manual shaking (Fig. 6). Other polyampholyte microgels **3c**–**e**, **4b**, **5a**,**b**, **6a**,**b**, and **7b** had a similar behavior, while lightly cross-linked microgels **3a**,**b**, **4a**, and **7a** exhibited only weak emulsifying properties at pH7.5. This is presumably because the polysaccharide interfacial films formed at basic conditions cannot prevent coalescence of oil droplets due to the weak interaction between microgel particles [22]. Appearance of unstable droplets and macroscopic phase separation follow this process. Optical microscopy studies recorded during the in situ addition of NaOH confirmed that rapid droplet coalescence occurred in the system. It should be noted that demulsification process is reversible and essentially the same droplet diameter was obtained after the addition of HCl followed by intensive shaking. Presumably, this is because these samples, for example **5b**, have high density of amino groups on their surface providing ionic repulsion at low pH. On the other hand, carboxyl groups of polysaccharide chains get combined in acidic media leading to the dynamic network of microgel

Table 3 Average diameter of oil droplets in emulsions on the basis of samples **3**–**7** (27 % of cross-linking density) at pH2 after 24 h

Sample	Average diameter of oil droplets (μm)		
	Toluene	Chloroform	Heptane
3d	30±2	25±2	62±3
4b	19±2	20±2	47±3
5b	14±2	17±2	44±3
6b	16±2	22±2	52±3
7b	28±3	34±3	55±3

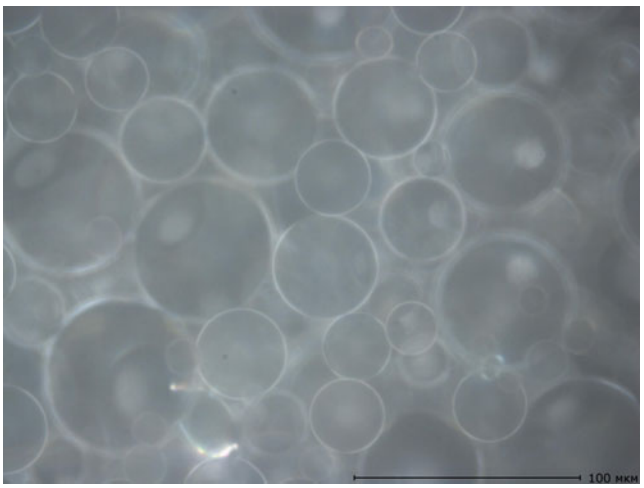


Fig. 5 Toluene-in-water emulsion of cross-linked microgel **5b**

Fig. 6 Formation of toluene-in-water emulsion of cross-linked microgel **5b** at pH8.5 (left tube) and pH2 (right tube)

particles on the oil–water interface. We propose, on the analogy of published results [22], that the formation of stable oil-in-water emulsions on the basis of pectinic acid modified with Ugi reaction is a result of interaction between particles of microgels, which can form an elastic film at the oil–water interface of an oil droplet (see supporting information). Moreover, elastic interfacial films are good protection against coalescence of oil droplets in emulsion. Hence, introduction of amino groups in the structure of apple pectin clearly enhances its emulsifying properties.

Conclusion

A novel method for the synthesis of polysaccharide microgel via Ugi multicomponent reaction has been developed. The process only used products generally regarded as safe and was controlled, in terms of size and size distribution, by both external (synthesis process) and internal (polymer characteristics) parameters. With pH and temperature set at optimum values, the concentration of the polymer in the solution and the cross-linkage density have been varied to obtain a maximal amount of particles per batch, with controlled colloidal properties. Increasing the degree of cross-linking leads to a polyampholyte microgel, which can be protonated in acidic medium or deprotonated in basic medium.

Polyampholyte microgels of pectinic acid with the high degree of cross-linking exhibit strongly pronounced emulsifying properties in acidic media and at low concentrations (ca. 1 g/l). This behavior is attributed to the formation of Pickering-like emulsions, which are stabilized by the adsorption of colloidal aggregates to the interfaces. The rapid demulsification occurs in the system after addition of NaOH at pH9–10 that opens the way to the rational design of pH-responsive emulsifiers on the basis of natural polysaccharides.

Stability of oil-in-water emulsions with polyampholyte microgels of pectinic acid depends largely on pH. Thus, stable emulsions are formed in the pH range 2–3, while at basic conditions instable interfacial films are observed. In addition, the strong interaction between carboxyl groups in polymer chains at low pH provides the formation of thick interfacial films on the water–oil boundary. Works in progress should allow us to determine the structure of these interfacial films using atomic force microscopy.

Acknowledgments The authors thank the members of the center "Modern Nanotechnology" at Ural Federal University for their assistance in DLS and the members of the laboratory "Comprehensive investigation and expert judgment of organic materials" at Ural Federal University for NMR measurement. VAB thanks the Russian Foundation for Basic Research (grants no. 11-03-00579-a).

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